Sodium Rivals Silver as Single-Atom Active Centers for Catalyzing Abatement of Formaldehyde

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ABSTRACT: The development of efficient alkali-based catalysts for the abatement of formaldehyde (HCHO), a ubiquitous air pollutant, is economically desirable. Here we comparatively study the catalytic performance of two single-atom catalysts, Na1/HMO and Ag1/HMO (HMO = Hollandite manganese oxide), in the complete oxidation of HCHO at low temperatures, in which the products are only CO2 and H2O. These catalysts are synthesized by anchoring single sodium ions or silver atoms on HMO(001) surfaces. Synchrotron X-ray diffraction patterns with structural refinement together with transmission electron microscopy images demonstrate that single sodium ions on the HMO(001) surfaces of Na1/HMO have the same local structures as silver atoms of Ag1/HMO. Catalytic tests reveal that Na1/HMO has higher catalytic activity in low-temperature oxidation of HCHO than Ag1/HMO. X-ray photoelectron spectra and soft X-ray absorption spectra show that the surface lattice oxygen of Na1/HMO has a higher electronic density than that of Ag1/HMO, which is responsible for its higher catalytic efficiency in the oxidation of HCHO. This work could assist the rational design of cheap alkali metal catalysts for controlling the emissions of volatile organic compounds such as HCHO.

INTRODUCTION

Formaldehyde (HCHO), emitted from building and furnishing materials, is one of the main indoor pollutants that is harmful to human health. Furthermore, it can also take part in some important atmospheric processes and contributes to photochemical pollution and catalytic ozone destruction. Therefore, it is crucial to control the HCHO emission. Heterogeneous catalytic oxidation of HCHO over transition metal oxides or supported metal catalysts is one of the most promising technologies, because efficient catalysts can convert HCHO into CO2 and H2O. Often, supported noble metal catalysts show much higher catalytic activity in HCHO oxidation than transition metal oxides, and hence attract great attention, but they are very expensive. To reduce the cost of noble metal catalysts, two strategies are often used: to improve the dispersion degree of noble metals, and to strengthen the metal-support interactions. Highly dispersed Pt catalysts with a low Pt loading showed excellent catalytic performance in the complete oxidation of HCHO at low temperatures. Surface-confined atomic silver catalysts with strong metal-support interactions enhanced catalytic efficiency for HCHO removal.

An appealing alternative is to use alkali metals to enhance the performance of noble metal catalysts in catalytic oxidation. For instance, Zhang et al. improved the catalytic activity of Pt/TiO2 or Pd/TiO2 by adding sodium, and they attributed the enhancement of catalytic activity to the increase of adsorbed OH groups active for HCHO oxidation. Similar results were reported by Nie et al. Bai et al. used potassium to enhance the performance of Ag/Co3O4 for HCHO abatement. These authors believed that alkali ions only serve as promoters. Likewise, a single Pt atom surrounded by six potassium atoms to form a PtK6 octahedron with a Pt core could facilitate the activation of oxygen species in the water–gas shift reaction. Although all surface atoms are K atoms, the authors still believed that the core Pt atoms are active sites.

The promotion effect of alkali metals has been reported in many catalytic reactions, especially in the synthesis of ammonia and the Fischer–Tropsch reactions. Occasionally, alkali ions can also promote oxide catalysts. Although noble metals often show higher catalytic activity than alkali metals in many reactions, alkali (or alkaline earth) metals atomically dispersed on the supports’ surfaces can be very active in some
catalytic oxidation.\textsuperscript{21,22} For example, isolated Ca\textsuperscript{2+} sites in hydroxyapatite tunnels were reported to be highly active for HCHO oxidation.\textsuperscript{23} Single-site K\textsuperscript{+} catalysts were found to be active for HCHO abatement because the K\textsuperscript{+} ions with the hybridized d-\textit{sp}\textsuperscript{3} orbitals showed significant activation ability toward both gaseous oxygen and lattice oxygen.\textsuperscript{22} Therefore, it is vital to differentiate the function of alkalis from that of noble metals under identical conditions.

In this work, we comparatively study the single-atom sodium and silver catalysts by anchoring single sodium or silver on the (001) surfaces of Hollandite manganese oxide (HMO), to shed light on the functions of alkali metals (Scheme 1). Synchrotron X-ray diffraction (SXRD) patterns with a structural refinement and transmission electron microscopy (TEM) images with energy dispersive X-ray spectroscopy (EDX) mapping are used to determine the location of the sodium or silver atoms. Catalytic performance of the single-atom catalysts in HCHO oxidation is studied. The electronic states and the metal–support interactions are revealed by X-ray absorption spectra and X-ray photoelectron spectra (XPS). This work assists the rational design of cheap alkali metal catalysts for controlling the emissions of volatile organic compounds (VOCs) such as HCHO.

\section*{EXPERIMENTAL SECTION}

\textbf{Catalyst Preparation.} The synthesis of samples was reported in our recent work.\textsuperscript{11,23} Briefly, HMO was prepared by a refluxing route and the resulting powders were calcined in air at 400 °C for 4 h (see details in the Supporting Information, SI).\textsuperscript{23} Ag\textsubscript{Ag}/HMO was first prepared by using the redox reactions,\textsuperscript{12} dried at 80 °C for 24 h, and calcined at 400 °C in air for 4 h to get Ag\textsubscript{Ag}/HMO (see details in the SI). The atomic ratio of Ag/Mn is ~0.15 for Ag\textsubscript{Ag}/HMO, as determined by using X-ray fluorescence spectrometer (XRF) on a Bruker-AXS S4 Explorer. NaCl/HMO was prepared by impregnating HMO powders with an aqueous solution of NaCl, followed by being annealing NaCl/HMO at 400 °C for 12 h and then washing the powder by deionized H\textsubscript{2}O at room temperature. The atomic ratio of Na\textsubscript{Na}/Mn is ~0.18 for Na\textsubscript{Na}/HMO, as determined by using XRF.

\textbf{Catalytic Evaluation.} The complete oxidation of HCHO was performed in a fixed-bed quartz reactor (i.d. = 8 mm) under atmospheric pressure. For each run, the reaction temperature began at room temperature, and was increased to the specified temperature at a rate of 1 °C min\textsuperscript{−1}. After holding the temperature for 1 h, the steady state would usually be reached, and the temperature would be held for another half an hour for data collecting. A fresh catalyst (50 mg, 40–60 mesh) was charged for each run. HCHO was generated by passing N\textsubscript{2} over paraformaldehyde (96%, Acros) in an incubator kept at 45 °C. The HCHO gas was mixed with flowing O\textsubscript{2} to get a feed gas (100 mL min\textsuperscript{−1} containing 140 ppm of HCHO, 10.0 vol % O\textsubscript{2}, and balance N\textsubscript{2}. For kinetics analysis, the X\textsubscript{HCHO} is kept below 20%. Turnover frequency (TOF) is defined as the number of HCHO molecules converted per active site per second (see details in the SI).

\textbf{Catalyst Characterizations.} SXRD patterns were recorded at BL14B of the Shanghai Synchrotron Radiation Facility (SSRF) at a wavelength of 0.6883 Å. Rietveld refinements of the diffraction data were performed with the FULLPROF software package on the basis of the space group I\textsubscript{4}/m, TEM, high-resolution TEM (HRTEM), and scanning TEM (STEM) with EDX mapping were conducted on a JEM 2100F transmission electron microscope. XPS were collected using the Kratos Axis Ultra-DLD system with a charge neutralizer and a 150 W Al (Monochromatized) X-ray gun (1486.6 eV) with an energy resolution of ~0.15 eV. The spectrometer was equipped with a delay-line detector. Spectra were acquired at normal emission with a passing energy of 40 eV. XPS data were referenced to the C 1s peak at the binding energy (BE) of 284.6 eV. Data analysis and processing were undertaken using the XPSPeak4.1 software with the Shirley type background. The soft X-ray absorption spectra at the O K-edge were measured in a total electron yield (TEY) mode at the 4B7B of the Beijing Synchrotron Radiation Facility (BSRF).

\textbf{Density Function Theory (DFT) Calculations.} DFT calculations were performed using the Vienna ab initio simulation package (VASP).\textsuperscript{24,25} The electronic structure of all the configurations was calculated using the generalized gradient approximation (GGA).\textsuperscript{26} The primitive cell of the NaCl crystal was used, and the optimized parameter is 3.999 Å,\textsuperscript{28} and an 8 × 8 × 8 k-point mesh was used for the relaxation. The lattice parameters (9.808 × 9.808 × 2.866 Å\textsuperscript{3}) of the Na\textsubscript{Na}/HMO crystal with the tetragonal space group I\textsubscript{4}/m were used according to the experimental data (Tables S1 and S2). The (001) surface of Na\textsubscript{Na}/HMO was cut based on the super cell with 36 included formula units, and an 3 × 3 × 1 k-point mesh was used for the static self-consistent calculations. The density of states (DOS) of the NaCl primitive cell and the (001) surface of Na\textsubscript{Na}/HMO were calculated.
RESULTS AND DISCUSSION

Structures of Single-Atom Catalysts. The tunnel openings on the (001) surfaces of HMO proved to be the catalytically active sites in the HCHO oxidation, because their size (0.26 nm) was close to the thermodynamic diameter of HCHO molecule (0.24 nm). Hence, depending on the types, electronic states, and precise positions, atoms anchored on the tunnel openings have an important influence on the catalytic reactivity of HMO. Silver atoms anchored on the HMO tunnel openings prepared by different methods have different electronic states, and thus they had different catalytic efficiency in HCHO oxidation. The greater depletion of the electronic states, and thus they had different catalytic activity. Silver atoms anchored on the tunnel openings have an important influence on the catalytic activity of HMO, because their side-facets often serve as catalytically active sites for the removal of some VOCs. After loading sodium or silver, the rod-shaped morphology of HMO remains unchanged, and the top-facets for both samples are exposed (Figure 2). Two

To identify the precise positions of Na and Ag on the tunnel openings, SXRD patterns of Ag1/HMO and Na1/HMO were collected and Rietveld refinement analyses were conducted (Figure 1). The structural models (insets in Figure 1) were constructed according to the corresponding lattice parameters and partial atom coordinates listed in Tables S1 and S2, respectively. A HMO model constructed from the SXRD pattern and refinement (Figure S1 and Tables S1 and S2) shows that HMO has one-dimensional square tunnels of 4.7 Å × 4.7 Å, and a narrow position of the tunnel is located at the (002) plane, which consists of 4 oxygen atoms (red balls in Figure S1) to form a square cavity. This square cavity is suitable for anchoring metal atoms such as sodium and silver at the center of the square, i.e., the position is the Wyckoff 2a sites. According to the refinement results (Table S2), both sodium and silver ions are situated at the same positions in the HMO tunnels. Thus, it is convenient to compare the catalytic activity of the single Na active centers with the single Ag active centers.

To investigate the influence of the incorporation of sodium or silver on the morphologies of HMO, we obtained the TEM and HRTEM images of HMO, Na1/HMO, and Ag1/HMO. In Figure S2, HMO grows along the tunnel direction or the [001] axis to form a rod structure, indicating that the surface energy of the (001) top-facets is much higher than that of the (100) side-facets. Thus, the tunnel openings on the (001) top-facets often serve as catalytically active sites for the removal of some VOCs. After loading sodium or silver, the rod-shaped morphology of HMO remains unchanged, and the top-facets for both samples are exposed (Figure 2). Two

fringes with a cross angle of 60° can be assigned to the (300) and (211) planes of both Na1/HMO (Figure 2a) and Ag1/HMO (Figure 2c), as confirmed by the corresponding fringe distances of 3.3 and 2.4 Å. Na1/HMO and Ag1/HMO can be more accurately written as Na1.5Mn8O16 and Ag1.2Mn8O16, respectively, according to the XRF analyses, which indicates that the molar fraction of Na is similar to that of Ag in HMO. The high dispersion of Na or Ag species is confirmed by EDX mapping (Figure 2b,d), and the distribution of Na or Ag on the ends of the rods is also detected, in line with the fact that the high active tunnel openings of the (001) top-facets are very suitable for anchoring metal ions such as alkalis and Ag.

The immediate structures of anchored Ag atoms were investigated using extended X-ray absorption fine structure (EXAFS) spectroscopy. Ag K-edge Fourier transform (FT) EXAFS spectra of the samples are shown in Figures S3, and Figure S4 gives the curve-fitting of R-space and inverse FT spectra. The related structural parameters obtained by fitting the spectra with theoretical models are listed in Table S3. The first amplitude of the EXAFS spectrum of Ag1/HMO is assigned to the Ag−O bonds with an average bond length of ~2.33 Å and a coordination number of 4. The results are in line with the refinement of the corresponding XRD pattern, demonstrating that Ag atoms are at the Wyckoff 2a sites. Likewise, the data also agree fairly well with the fact that Ag atoms are stably fixed on the (002) plane to form planar AgO4−.
Because the Na K-edge EXAFS spectrum appears at significantly low absorption energies, the immediate environment of the anchored Na on the HMO planes is not obtained from its EXAFS spectrum. However, previous work with experimental and theoretical results demonstrated that sodium ions are energetically favorable to locate at a “bottleneck” on the (002) plane to form NaO$_4$ structural motifs, similar to the AgO$_4$ motifs. As a consequence, the sodium and silver atoms are located at almost the same vacant sites on the (002) facets.

**Catalytic Oxidation of HCHO.** Two single-atom catalysts together with HMO were used to catalyze HCHO oxidation, because HCHO is a typical pollutant in indoor air, and it can also contribute to atmospheric particulate emissions in severe haze events. Our previous work reported that the tunnel openings of HMO function as catalytically active sites in the complete oxidation of HCHO. Owing to the suitable size of the tunnel opening similar to the diameter of the HCHO molecule, HMO often gives better catalytic performance than $\beta$-MnO$_2$ and todorokite manganese oxides under identical conditions.

As shown in Figure 3a, at a high GHSV of 92 000 h$^{-1}$, the $X_{\text{HCHO}}$ over HMO is $\sim$20% at 110 °C. The $X_{\text{HCHO}}$ increases drastically with further increasing reaction temperature, and complete oxidation of HCHO is achieved at 140 °C. Similar results were reported in the related work. After anchoring the Na or Ag atom at the tunnel openings of HMO, the catalytic activity distinctly increases. Especially, Na$_1$/HMO shows much higher catalytic activity than Ag$_1$/HMO. The temperature required for 20% $X_{\text{HCHO}}$ decreases to 90 °C, and 100% $X_{\text{HCHO}}$ is achieved at 110 °C over Na$_1$/HMO, while complete conversion of HCHO for Ag$_1$/HMO occurs at 130 °C. Likewise, we recently found that single potassium ions anchored on the tunnel openings of HMO showed the same catalytic performance as Na$_1$/HMO. The data thus indicate that single alkali atoms can be more active than single silver atoms in catalytic oxidation of HCHO.

It has been proven that the tunnel openings of HMO serve as the catalytically active centers in HCHO oxidation. Three samples should have the same number of catalytically active centers per unit manganese in mole, because the exposed sodium and silver atoms are anchored on the tunnel openings of the HMO rods. Thus, we plot an Arrhenius profile, and give the pre-exponential factors (Γ) of the reaction to estimate the number of possible active centers. Although the number of sodium atoms in Na$_1$/HMO is almost the same as that of Ag atoms in Ag$_1$/HMO, and it is also similar to the number of the tunnel openings of HMO, the Γ values of Na$_1$/HMO (∼1.5 × 10$^{18}$) and Ag$_1$/HMO (∼2.1 × 10$^{18}$) are much larger than that of HMO (∼5.9 × 10$^{15}$), implying that the accurate active centers for Na$_1$/HMO and Ag$_1$/HMO should include the surface active oxygen ions in contact with or in the periphery of sodium or silver atoms. The catalytic performance of these catalysts is intimately associated with the surface lattice oxygen ions (O$_x$) at the periphery of sodium and silver atoms, and these O$_x$ with nucleophilic properties are favorable to attack HCHO with the electrophilic carbonyl group. According to our recent report, 0.7% O$_x$ with respect to total lattice oxygen atoms are active for HCHO oxidation. Luo et al. reported similar findings that 0.3% O$_x$ of HMO are responsible for complete oxidation of organic compounds. Moreover, the electronic states of O$_x$ also play an important role in determining catalytic performance. As a consequence, two crucial factors governing the catalytic activity are the number and the electronic states of O$_x$. As shown in Figure 3, Na$_1$/HMO has the best catalytic performance and the largest Γ, possibly indicating that Na$_1$/HMO has more O$_x$ available for the HCHO oxidation than the other two samples.

**Activity-Structure Correlations.** We further studied the electronic properties of lattice oxygen, manganese, and sodium and silver atoms, to correlate the structures with catalytic performance. O 1$s$ XPS were collected to investigate the electronic density of O$_x$ (Figure 4a). An intensive peak at a low BE of $\sim$528 eV with a shoulder at a relatively high BE of $\sim$531 eV is observed for three samples. The low BE peak should be ascribed to the O$_x$ that is nucleophilic. A differential XPS of Na$_1$/HMO by subtracting the XPS of Ag$_1$/HMO appears with a negative peak in the high BE regime and a positive peak in the low BE regime, evidencing that the electronic density of O$_x$ of Na$_1$/HMO is higher than that of Ag$_1$/HMO. Thus, it has stronger nucleophilic properties, which leads to an easier reaction with electrophilic carbonyl group and further facilitates HCHO oxidation.

Furthermore, Zhang et al. has found that the O 2$p$ orbitals play an important role in determining the catalytic activity. Soft X-ray absorption spectra at the O K-edge were used to differentiate the electronic structures of O between Na$_1$/HMO and Ag$_1$/HMO, reflecting the interactions between O and sodium or silver. Figure 4b shows the normalized soft X-ray absorption spectra of Na$_1$/HMO, Ag$_1$/HMO, and HMO. Three spectra exhibit two main peaks centered at $\sim$527 and $\sim$529 eV, which can be attributed to the transition from the O 1$s$ orbitals into the $t_{2g}$ and $e_g$ orbitals, respectively. The high energy peak intensity of Na$_1$/HMO with the $e_g$ feature is slightly weak with respect to that of HMO, indicating that the occupied states of the O 2$p$ orbitals with the $e_g$ feature of Na$_1$/HMO increase. On
the contrary, the O 2p orbitals with the $e_g$ feature of Ag/HMO have the electronic density lower than those of HMO, as judged by the fact that the intensity of Ag/HMO at the high energy is much stronger than that of HMO. Hence, the O$_2$ of Na/HMO has the O 2p orbitals with the high electronic density, which should be an important factor to determine the catalytic performance in the complete oxidation of HCHO.

To clarify the reasons why O$_2$ of Na/HMO have higher density than those of Ag/HMO, the electronic properties of Na or Ag and Mn were investigated. The electronic states of Mn in three samples in terms of the average oxidation state (AOS) of Mn were estimated by Mn 2p and Mn 3s XPS data. As shown in Figure S5, the Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ peaks are centered at $\sim$641.9 and $\sim$653.6 eV, respectively, with an energy span of $\sim$11.7 eV, implying that the Mn species are predominately Mn$^{4+}$ for three samples.$^{40}$ To more accurately determine the AOS of Mn, the Mn 3s XPS are also shown in Figure S6. According to an energy difference ($\Delta E_{3s}$) between the main peak and its satellite of the Mn 3s XPS, and a relationship between the $\Delta E_{3s}$ and the AOS of Mn,$^{41}$ the same AOS of Mn for all cases can be calculated to be $\sim$3.8. In our previous studies,$^{11,31,32}$ the Ag atoms in Ag/HMO lose part of electrons and remain at the metallic states (Ag$^{\delta+}$, $0 < \delta < 1$). The electronic states of Na were determined by Na 1s XPS spectra (Figure S5a). The BE of the Na 1s peak shifts upward by $\sim$0.6 eV for Na$_2$/HMO with respect to that of NaCl, i.e., from 1070.6 eV for NaCl to 1071.2 eV for Na$_2$/HMO. This indicates that the isolated sodium atoms in Na$_2$/HMO have lower electronic density than those in NaCl. These results indicate that the different electronic states of the surface lattice oxygen predominantly originate from the interactions of O with Na or Ag.

Generally, HCHO oxidation on metal-supported transition metal oxides follows the metal-assisted Mars-van Krevelen mechanism,$^{42}$ in which a two-stage redox process takes place: (1) the dissociation of molecular oxygen (O$_2$) to form O$_2^-$ and (2) the oxidation of HCHO or adsorbed formate (the stable intermediate in the HCHO oxidation reaction) by O$_2^-$.  

$$
\text{O}_2 + 2(\cdot) \rightarrow 2(\text{O}_2^-) \\
\text{HCHO} + (\text{O}_2^-) \rightarrow (\text{HCOO}) \\
(\text{HCOO}) + (\text{O}_2^-) \rightarrow (\text{CO}_2^-) + (\text{H}_2\text{O})$$

where (·) represents an active site. Therefore, the mobility and reducibility of the O$_2^-$ are of crucial importance. The above results indicate that the O$_2^-$ of Na$_2$/HMO has higher electronic density, especially in the O 2p orbitals, indicating that the reducibility of the O$_2^-$ is improved, which will enhance the catalytic activity. Furthermore, it has been proven that the higher electronic density of the O$_2^-$ of Na$_2$/HMO originates from Na, not from Mn, showing a strong interaction between Na and O. The DOS of Na 3p orbitals were calculated as shown in Figure 5b. After the Na was anchored on the HMO(001) surfaces, the band gap between the lowest unoccupied molecular orbitals (LUMO) and the highest occupied molecular orbitals (HOMO) narrowed, suggesting that the electron transfer between Na and O is expected to become relatively easy.$^{43}$ Moreover, the DOS at HOMO of Na$_2$/HMO is relatively lower than that of NaCl, indicating that the electron transfer from Na to O occurred. This is consistent with the XPS results in Figure 5a. Therefore, sodium on the tunnel openings of HMO reduces the band gap between LUMO and HUMO and increases the reducibility of the O$_2^-$, thus being favorable for HCHO oxidation.

In conclusion, single-atom sodium and silver catalysts were synthesized by anchoring single sodium or silver atoms on the (001) surfaces of HMO, as evidenced by SXRD patterns with a structural refinement and TEM images with EDX mapping.
Na$_x$/HMO exhibited higher catalytic activity in the complete oxidation of HCHO than Ag$_x$/HMO. The results demonstrated that the catalytically active centers include the surface single sodium or silver and the vicinal lattice oxygen atoms, and that the electronic states of the surface lattice oxygen play a critical role in determining the catalytic performance in HCHO oxidation. The surface lattice oxygen species of Na$_x$/HMO with more negative charge had stronger nucleophilic properties, thus oxidation. The surface lattice oxygen species of Na$_x$/HMO with sodium or silver and the vicinal lattice oxygen atoms, and that Co$_3$O$_4$-CeO$_2$ catalysts at room temperature: Effective removal and alkali active sites for air purification.

**Associated Content**

**Supporting Information**

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Related tables and figures showing crystallographic data and parameters (PDF)

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**Notes**

The authors declare no competing financial interest.

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